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Bis(dioxaborine) Dyes with Variable π -Bridges: Towards Two-Photon Absorbing Fluorophores with Very High Brightness

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Abstract: Bis(dioxaborine) dyes of the A- π -A format (A: acceptor, π : conjugated bridge) were prepared and photophysically characterized. The best performing dyes feature (a) visible-light absorption (>400 nm), (b) high molar absorption coefficients (up to 70000 M⁻¹cm⁻¹), (c) Stokes shifts in the range of ca. 2500-5500 cm⁻¹, and (d) strong fluorescence emission with quantum yields of up to 0.74. This yields very bright-emitting dyes for one-photon excitation. However, the most intriguing feature of the dyes is their strong two-photon absorption. This was achieved by means of increased π -conjugation in the phenylene or phenylene-thiophene bridges through the variation of the conjugation length and rigidity. This provided twophoton absorption cross sections of up to 2800 GM (1 Goeppert-Mayer (GM) = 10^{-50} cm⁴ s photon⁻¹). Considering the mentioned high fluorescence quantum yields, exceptionally bright emitting A-n-A two-photon absorbing dyes with low molecular mass are obtained. Time-dependent density-functional theory calculations corroborated the experimental results.

Introduction

In recent years boron-containing molecular organic architectures have attracted elevated interest because of their photophysical properties, such as strong light absorption and emission.^[1-3] This is reflected in high brightness, being the product of the molar absorption coefficient and the emission quantum yield. If these properties are combined with light absorption at wavelengths longer than 400 nm and emission in the spectral region >500 nm, as well as significant Stokes shifts, then dyes with potential in bioimaging or optoelectronic applications are identified.^[2, 4-6] There are several examples of organoboron dyes that fulfil these

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ideal requirements to a large extent.^[1, 3, 7-19] An additional asset would be the capacity of dye to be stimulated in a two-photon excitation process.^[20-22] This creates the same emissive state as conventional one-photon excitation, but makes use of nearinfrared (NIR) photons. These are of low energy and in general spectrally well separated from the emitted light, thereby avoiding eventual experimental issues due to straylight or photodegradation. These features have been especially valued applications that imply imaging in by fluorescence microscopy.[23-26]

In front of this background there has been much progress in the tailored design of molecular architectures that feature high two-photon absorption (TPA) cross sections.[26-31] The most popular approaches are based on π -conjugated dipolar donoracceptor architectures (D- π -A) or centrosymmetric quadrupolar π -conjugated dyes with terminal donor or acceptor substitution $(D-\pi-D, A-\pi-A, D-A-D, A-D-A)$. The design strategies build on the variation of the conjugation length and the control of intramolecular charge redistribution on excitation, either from D to A or between the center and the A/D substituted ends of the molecule. However, there is room for improvement because dyes with high cross sections feature very often high molecular weights and imply elevated synthetic labour. In addition, so far reported A- π -A architectures show generally inferior TPA performance as compared to dyes that incorporate donor moieties.



Scheme 1. Strategies for improving the TPA properties of bis(dioxaborine) dyes and structures of the herein investigated dyes 1–7.

Recently, we have reported tetracoordinate borylated arylisoquinolines and boronic-acid derived dyes that show significant TPA cross sections (up to 300 GM, 1 GM = 10^{-50} cm⁴ s $photon^{-1}$).^[14, 32] In the present work we have focused on bis(dioxaborines), another class of tetracoordinate organoboron dyes. Previous studies have demonstrated that they are interesting candidates for organic electronics,[33-36] non-linear optical materials,[37, 38] as TPA dyes,[39-43] and as fluorescent probes.^[43-45] The dioxaborine moiety is a strong electronacceptor unit and so far reported dyes are of the abovementioned A-n-A or A-D-A format. It was shown that the A- π -A bis(dioxaborines) dyes show significant TPA cross sections of up to 500 GM for excitation with visible light around 600 nm.^[39-41] For bis(dioxaborines) with a carbazole as electrondonor bridge high TPA cross sections (530 GM) were measured for excitation at 700 nm.^[39, 41] Bis(dioxaborines) with biphenylene bridges (either flexible or rigidified) show also some TPA activity for excitation longer than 700 nm. but unfortunately with rather modest cross sections (ca. 10-20 GM). [40, 41] With the idea to improve the TPA features in the NIR region we oriented towards the further extension of the conjugation length, combined with increased planarization or the electronic integration of thiophenes (see structures in Scheme 1). Indeed, we were able to show a dramatic increase of the TPA cross sections to values of about 2000-3000 GM for excitation in the 700-800 nm NIR spectral region. This observation and the generally high emission quantum yields propose some of the herein investigated compounds as very bright-emitting TPA dyes.

Results and Discussion

Synthesis of bis(dioxaborines)

The bis(dioxaborine) dyes 1-7 were synthesized from acetylated aromatic compounds by treatment with BF₃-CH₃COOH complex according to reported protocols for related dyes.^[46] The isolated yields were 86-96%, except for dye 1 (71% yield). Noncommercial acetylated aromatic compounds were prepared by direct double Friedel-Crafts acetylations of the parent hydrocarbon, or by standard Suzuki or Ullmann coupling reaction of acetylated precursors. The detailed experimental procedures and analytical data can be found in the Supporting Information.

One-photon optical properties

The bis(dioxaborines) 1-7 were characterized with respect to their one-photon UV/vis-absorption (OPA) and fluorescence properties in acetonitrile solution. The corresponding data are summarized in Table 1 and the spectra are shown in Figure 1 and 2. Generally it can be affirmed that the investigated dyes are strong absorbers with long-wavelength maxima in the spectral range between ca. 370 and 440 nm, featuring molar absorption coefficients (ε) as high as 70000 M⁻¹cm⁻¹. The fluorescence of the dyes was observed in the blue to green-yellow spectral range (maxima between 413 and 535 nm) and shows maximum

quantum yields of 0.6–0.7. Consequently, the brightness ($\varepsilon \times$ Φ_{fluo}) of some of these dyes is very high,^[19] reaching values of about 42000-46000 M⁻¹cm⁻¹ for the bis(dioxaborines) 2-4. and highly advantageous These interesting characteristics are complemented by Stokes shifts of ca. 2500-5600 cm⁻¹ and fluorescence lifetimes in the range of 1-4 ns (except for dye 1). The herein observed Stokes shifts are comparable to those obtained for other boron(III) dye architectures with heterocylic ligands.^[3] The absolute values are indicative for significant electronic rearrangements on excitation.

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| Table 1. Photophysical data of the bis(dioxaborine) dyes 1-7 in aerated acetonitrile. $^{\rm [a]}$ | | | | | | | | |
|--|--|--|----------------------|--|---|--------------------------------|--|--|
| | $\lambda_{abs,max} (nm) \ [arepsilon (M^{-1}cm^{-1})]^{[b]}$ | λ _{fluo,max} (nm) ^[c] | $arPsi_{fluo}^{[d]}$ | τ _{fluo} (ns) ^[e] | Stokes shift (cm ⁻¹) ^[f] | $\delta \left(GM\right)^{[g]}$ | | |
| 1 | 363 [37000] | 418 | 0.18 | < 0.2 | 3678 | [h] | | |
| 2 ^[i] | 370 [71000] | 413 | 0.61 | 0.92 | 2864 | 20 [700] 12 [770] | | |
| 3 | 377 [57000] | 479 | 0.74 | 1.60 | 5645 | 744 [700] 109 [750] | | |
| 4 | 440 [68000] | 506 | 0.67 | 2.52 | 2951 | 2800 [730] 337 [890] | | |
| 5 | 442 [55000] | 496 | 0.45 | 1.59 | 2462 | 1674 [710] 45 [880] | | |
| 6 | 428 [48000] | 535 | 0.67 | 2.03 | 4706 | 2002 [730] 200 [890] | | |
| 7 | 440 [47000] | 506 | 0.35 | 4.13 | 3922 | 1684 [770] 106 [880] | | |

[a] Compound 3 required the addition of 0.3 vol% DMF. The TPA measurements were done with DMF as additive (0.2 vol%, except for dye 3 where 2.4 vol% were used. [b] Longest-wavelength absorption maximum, in square brackets the corresponding molar absorption coefficient is given. [c] Fluorescence emission maximum. [d] Fluorescence emission quantum yield; 15% error. [e] Fluorescence lifetime measured by time-correlated singlephoton-counting; 5% error. For the compounds 4-7 multiexponential decays were registered and the lifetime of the most dominant contribution is given. [f] The corresponding energies in eV are: 0.46 (1), 0.36 (2), 0.70 (3), 0.37 (4), 0.31 (5), 0.58 (6), 0.49 (7). [g] TPA cross sections were measured in the range of 700-1000 nm; in square brackets the corresponding TPA wavelength is provided. The highest cross section and the one corresponding to the longest wavelength maximum are given. [h] No significant TPA properties were measured. [i] The UV/vis-absorption spectrum and emission quantum vield of an analogous compound, containing n-propyl instead of methyl, were reported for dichloromethane as solvent: $\lambda_{max,abs}$ = 373 nm, Φ_{fluo} = 0.68; ref. [39]. These data compare nicely with the herein obtained values for 2 in acetonitrile.

The investigated dyes can be divided into two sub-series regarding the variations of the π -bridge that connects the two dioxaborine moieties. Sub-series I contains the dyes 1-4 with para-phenylene linkers. These dyes show a systematic variation of their UV/vis-absorption and fluorescence maxima with increasing length of the bridge (1-3) and consequently increasing π -conjugation (Figure 1). Each addition of a para-

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phenylene yielded a bathochromic shift of the UV/vis-absorption maximum by 7 nm. Also for the fluorescence maxima a bathochromic shift was observed for the stepwise extension of the π -bridge, amounting to 82 nm when comparing the dyes **1** and **3**, with one and three phenylene units, respectively. The case of dye **4** is significant because the increased planarization of the bridge causes even higher π -conjugation. This leads to a further shift of the absorption and fluorescence maxima by 63 nm and 27 nm, respectively, compared to the terphenylene-bridged bis(dioxaborine) **3** with the same conjugation length; Figure 1.



Figure 1. UV/vis-absorption (black) and fluorescence spectra (red) of the dyes 1–4 in acetonitrile. The fluorescence spectra were obtained by excitation at the wavelength of maximum absorbance.



Figure 2. UV/vis-absorption (black) and fluorescence spectra (red) of the dyes 5--7 in acetonitrile. The fluorescence spectra were obtained by excitation at the wavelength of maximum absorbance.

Sub-series II is constituted by the compounds 5-7 with thiophene-containing bridges. These dyes feature absorption maxima at wavelengths longer than 400 nm, i.e., 430-440 nm, and emission maxima close to 500 nm and in some case even at ca. 540 nm (dye 6); Figure 2. Noteworthy, the substitution of one or two para-phenylene units by thiophene (dyes 2, 3 versus 5-7) yields significant bathochromic shifts of the UV/visabsorption and emission bands. These observations are reasoned with the higher π -conjugation in thiophene bridges as compared to phenylene bridges.^[47, 48] Interestingly, the connectivity of the thiophene in the bridge plays an important role. While the direct neighborhood of thiophenes to the dioxaborine moieties yields a red-shifted UV/vis-absorption maximum, the inclusion of thiophene as central part of the bridge red-shifts the emission maximum (compare dyes 6 and 7; Table 1). The emission quantum yields are moderate to high, being somewhat lower for the dyes that incorporate two thiophene units, i.e., 5 and 7.

The global photophysical trends are well reproduced by time-dependent density-functional-theory (TD-DFT) calculations [B3LYP/6-31+G(d)],^[49, 50] accounting for acetonitrile as solvent by including the polarization-continuum model (PCM); see Table 2. The S₁—S₀ excitation is dominated by the LUMO—HOMO transition. The same frontier orbitals are involved in the S₁—S₀ emission. Consequently, the experimental UV/vis-absorption and emission maxima follow the trend that is dictated by the HOMO–LUMO energy bandgap, being largest for dye 1 and smallest for the dyes with higher π -conjugation, i.e., 4–7. Once more, also the calculated bandgaps confirm nicely that the increased rigidity (dye 4) or the integration of the comparably stronger electron-donating thiophene as bridge element (dyes 5–7) increases the level of π -conjugation.

Two-photon absorption (TPA) properties

The most intriguing property of the herein investigated dyes are their TPA cross sections. In the present work the TPA characteristics between 700 nm and 1000 nm were studied by the method of two-photon-induced fluorescence (TPIF).^[51] In the context of TPA-active compounds with $D-\pi-D$, $A-\pi-A$, D-A-Dor A-D-A architecture, centrosymmetry is generally identified as a structural key element, while π -conjugation constitutes the electronic ingredient.^[29] Centrosymmetry is fulfilled for the conformations of the dyes **1**, **3**, **4**, and **5** that are shown in Scheme 1. Note for example that the lowest-energy groundstate conformations of these dyes, having the two dioxaborine units in *anti*-orientation, feature a dipole moment of practically zero Debye (see Table 2). More calculated structural data for the dyes **1**–**7** can be found in the Supporting Information.

The TPA spectra of the dyes **2–7** are shown in Figure 3. In line with the above discussed rationale, dye **3** has a significantly higher δ value than dye **2** (see Table 1). However, it was the locking of the bridge conformation in **4** that turned out to push the TPA cross section of bis(dioxaborines) beyond currently known literature values for A– π –A dyes with similar conjugation length, reaching 2800 GM at 730 nm. This observation combined with an emission quantum yield of 0.67 leads to the

conclusion that dye **4** belongs to the TPA A- π -A dyes with highest brightness ($\delta \times \mathcal{P}_{fluo}$; 1876 GM); see for comparison other dyes in the Supporting Information. Even for the longest-wavelength TPA maximum at 890 nm an appreciable cross

section of 337 GM was measured for dye **4**, being comparable to the performance of other boron-containing fluorescent architectures.^[14, 19-22]

| | | | | | | | | A | | _ | |
|-----|---|--|--|---|------------------|--|-----------------------------------|---|---|---|---|
| Tab | Table 2. Calculated electronic and photophysical data for the bis(dioxaborine) dyes 1–7. ^[a] | | | | | | | | | | |
| | Absorption | | | | Emission | | | | | | |
| - | f ^{b]} | Dominant component (%) ^[c] | $E_{ m max,calc}$ (eV) ^[d] | E _{max,exp} (eV) ^[d] | f ^[b] | Dominant component (%) ^[c] | $E_{ m max,calc}$ $(eV)^{[d]}$ | E _{max,exp} (eV) ^[d] | μ (S ₀) (D) ^[e] | μ (S ₁) (D) ^[e] | $\Delta E_{ m HOMO-LUMO}$ (eV) ^[f] |
| 1 | 1.050 | LUMO←HOMO (99) | 3.47 | 3.42 | 1.323 | LUMO→HOMO (100) | 2.82 | 2.97 | 0.01 | 0.01 | 3.89 |
| 2 | 1.605 | LUMO←HOMO (99) | 3.25 | 3.35 | 2.106 | LUMO→HOMO (99) | 2.55 | 3.00 | 5.55 | 1.15 | 3.69 |
| 3 | 1.704 | LUMO←HOMO (98) | 3.04 | 3.29 | 2.511 | LUMO→HOMO (99) | 2.35 | 2.59 | 0.00 | 0.01 | 3.47 |
| 4 | 1.807 | LUMO←HOMO (99) | 2.80 | 2.82 | 2.383 | LUMO→HOMO (99) | 2.33 | 2.45 | 0.00 | 0.01 | 3.17 |
| 5 | 1.437 | LUMO←HOMO (100) | 2.72 | 2.81 | 1.723 | LUMO→HOMO (100) | 2.10 | 2.50 | 0.22 | 2.46 | 3.08 |
| 6 | 1.701 | LUMO←HOMO (99) | 2.65 | 2.90 | 2.316 | LUMO→HOMO (99) | 2.03 | 2.32 | 5.98 | 7.92 | 3.04 |
| 7 | 1.734 | LUMO←HOMO (99) | 2.70 | 2.82 | 2.684 | LUMO→HOMO (99) | 2.01 | 2.45 | 3.09 | 2.10 | 3.10 |

[a] Calculated by TD-DFT (see text), corresponding to the $S_1 \leftarrow S_0$ transition (absorption) and $S_1 \rightarrow S_0$ transition (emission). [b] Oscillator strength. [c] Percentage contribution approximated by 2 x $(c_i)^2$ x 100%; c_i is the coefficient for the particular "orbital rotation". [d] Calculated (calc) and experimental (exp) energies. [e] Dipole moment in the ground state (S_0) and first singlet excited state (S_1). [f] HOMO-LUMO energy bandgap.



Figure 3. TPA spectra of the dyes 2 (black), 3 (red), 4 (dark blue), 5 (blue), 6 (green), and 7 (magenta) in acetonitrile. The spectra of dyes that belong to the sub-series I (2–4) are symbolized by filled circles and for sub-series II (5–7) empty circles are used.

The strategy of fine-tuning the π -conjugation of the bridge was also followed in sub-series II, consisting of the thiophenecontaining dyes **5–7**. A first hint on the improved conjugation of the bridge can be obtained by comparing the cross sections of the dyes **2** and **5**. Both have the same conjugation length, but the thiophene variant features a much higher TPA cross section (see Table 1 and Figure 3). The same observation applied for the dyes **6** and **7**, where in comparison to dye **3** one or two thiophenes substitute phenylene(s). This electronic variation yielded δ values of 2002 GM (at 730 nm) and 1684 (at 770 nm) for **6** and **7**, respectively. The associated brightness is somewhat affected for dye **7**, due to its lower emission quantum yield (see discussion above). However, dye **6** maintains a high emission quantum yield ($\Phi_{fluo} = 0.67$), giving rise to a brightness of 1341 GM (at 730 nm).

The dyes **4**, **6**, and **7** with the highest TPA cross sections in this work stand out among other D– π –D and A– π –A architectures with similar spectral positions of the TPA bands.^{[28, ^{29]} As an orientation we normalized the TPA cross sections for the number of π -electrons (N_e) in the conjugated bridge (∂N_e). Our best performing dyes feature values of *ca*. 70–110 GM per π -electron, while typical values for other A– π –A structures do not exceed 10–20 GM per π -electron. Even D– π –D dyes, that are known to have generally higher cross sections,^[29] do reach at best 50–75 GM per bridge π -electron; see comparison with literature-known systems in the Supporting Information.}

As a general observation for the investigated compounds, the most intense TPA bands (at *ca*. 720–770 nm) are not related to the transition that corresponds to the longest-wavelength OPA bands (see Figure 4). This suggests that the strongest TPA transitions implicate higher excited states, namely the S₂ state. In agreement the calculated energy of the S₂—S₀ transition divided by two compares quite well with the energy corresponding to the TPA wavelength maximum of the strongest band. At the same time the less strong TPA feature at wavelengths longer than 850 nm correlates well with the lowest energy transition (S₁—S₀); see Figure 4 for the examples of **4** and **6**.

Similar conclusions can be drawn from symmetry considerations. For the centrosymmetrical molecules **3**, **4**, and **5** the symmetry of the S₀, S₁, and S₂ states is A_g, A_u, and A_g, respectively. Thus, in accordance with the selection rules the oscillator strength of the S₂ \leftarrow S₀ transition is zero in the OPA process. This is reversed for the TPA process in centrosymmetric chromophores,^[29] and hence, the S₂ \leftarrow S₀ (A_g to A_g) transition is TPA-active for these dyes.



Figure 4. Comparison of OPA spectra (bottom) and TPA spectra (top) spectra of 4 (right) and 6 (left). The x-axis of the two-photon spectra was divided by 2, to allow a comparison.



Figure 5. NTO orbitals for the $S_1 \leftarrow S_0$ transition (bottom) and for the $S_2 \leftarrow S_0$ transition (top) for dye 4.

Natural transition orbitals (NTOs) are very appropriate to describe the electronic re-distributions in excitation events.^[29] The NTOs were calculated for the two lowest-energy transitions, i.e., $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$, providing a visualization of the electron and hole distributions. Figure 5 shows the NTOs of the best performing dye 4 (information on the other dyes can be found in the Supporting Information). On the one hand, it can be clearly seen that the hole is evenly localized on the bridge for both transitions. On the other hand, the electron is spread over the whole molecule for the $S_1 \leftarrow S_0$ transition. This situation is quite different for the $S_2 \leftarrow S_0$ transition, where the electron is concentrated at the acceptor ends of the dyes, thereby further increasing the quadropolar polarization. This picture explains well the variation of the TPA cross sections involving either S1 or S₂ (see experimental data and discussion above) and complements the conclusions that were drawn from the symmetry considerations (see above). The increased quadrupolar polarization applies as well to the non-centrosymmetrical dyes **6** and **7**, giving reason to their high TPA cross sections (see NTO analysis in the Supporting Information).

Conclusions

Bis(dioxaborine) dyes with varying degree of π -conjugation length and rigidity of the bridge element were prepared and photophysically characterized. As bridges phenylene, thiophene, or mixed phenylene-thiophene linkers were tested. In general the dyes show high fluorescence quantum yields, reaching 0.6–0.7, and are strong light absorbers. This gives rise to very high brightness (up to 46000 M⁻¹cm⁻¹) for one-photon excitation of some of the investigated dyes.

In cases where the bridge of the A– π –A architectures supports an extended π -conjugation (determined by rigidity, number of π -electrons, HOMO-LUMO gap) exceptionally high TPA cross sections δ were measured (up to 2800 GM), being among the highest that were so far observed for quadrupolar D– π –D and A– π –A architectures with similar conjugation and low molecular weight. The high emission quantum yields provide outstanding TPA-related brightness of up to 1900 GM to some of the investigated dyes. These dyes can be foreseen to find applications especially in optoelectronic materials.

Experimental Section

General synthetic procedures

General procedure for double acetylation. A solution of the aromatic compound (1 equiv) in dichloromethane was added dropwise during 20 min to a flask charged with a stirred mixture of anhydrous aluminium chloride (2.3 equiv) and acetyl chloride (2.1 equiv) in dichloromethane at 0 °C. The mixture was kept at 0 °C for 3 hours and then added to ice water, containing HCI. The precipitate was isolated by filtration and washed with copious amounts of water.

General borylation procedure. A flask was charged with a mixture of the acetylated aromatic compound (1 equiv) and acetic anhydride (3 equiv) and then heated to 45 °C under nitrogen atmosphere. Then a solution of BF₃-CH₃OOH complex (2 equiv) was added. The mixture was kept at 45 °C for additional 6 hours. Then, the mixture was filtered and the solid was washed with acetic acid, ethyl acetate, and diethyl ether.

Detailed information on the preparation of each dye and the analytical characterization can be found in the Supporting Information.

Photophysical measurements

Photophysical experiments were carried out at room temperature with aerated and optically diluted (absorbance at excitation wavelength *ca.* 0.1–0.2) acetonitrile solutions. The UV/vis-absorption spectra were recorded with a UV-1603 spectrophotometer (Shimadzu). The fluorescence spectra were obtained with a Cary Eclipse fluorimeter (Varian). Fluorescence excitation spectra, monitoring the emission maximum, were measured to confirm the identity of the observed

emissions. The fluorescence quantum yields were determined with 4amino-1,8-naphthalimide ($a_{fluo} = 0.48$ in acetonitrile)^[19] or quinine sulfate ($a_{fluo} = 0.55$ in 0.05 M H₂SO₄)^[52, 53] as reference and corrected for refractive index differences of the solvents for the sample and the reference. The lifetime measurements were performed by means of timecorrelated single-photon-counting (Edinburgh instruments FLS 920) with a picosecond pulsed UV-LED (EPLED 360, $\lambda = 367$ nm, pulse width fwhm 745 ps) or a picosecond pulsed laser diode (EPL 445, $\lambda = 442$ nm, pulse width fwhm 78 ps) as excitation source. The lamp profile was obtained with a light-scattering colloidal solution (Ludox).

The TPA cross sections (δ) were determined by the two-photon-induced-fluorescence method.^[51, 54] The dyes **2–7** were dissolved in acetonitrile (concentration of 10 µM), containing a small amount of *N*,*N*-dimethylformamide (0.2 vol%, except for dye **3**, where 2.4 vol% were used). The emission spectra were measured in 1 mm pathlength high-precision Suprasil quartz cells for two-photon excitation between 700 nm and 1000 nm with the aid of a Leica SP5 AOBS MP instrument, equipped with a MaiTai Ti:Sapphire HP laser (Spectra-Physics, Inc.). Rhodamine B was employed as reference (10 µM in methanol) under experimentally identical conditions, using $\sigma_{huo} = 0.71$ and $\delta = 210$ GM at 840 nm and a previously published method.^[24, 55] The measurements were done at laser powers that assured the occurrence of two-photon processes. In accordance, plots of log(emission intensity) *versus* log(laser power) yielded slopes of 2.0±0.1 in all cases.

DFT calculations

All calculations were done with the Gaussian 09 package.^[56] The geometry optimization was performed using density-functional theory (DFT) and the B3LYP functional^[57] together with the 6-31+G(d) basis set.^[58] For dye 4, the butyl chains were replaced by methyl groups, as it is expected that the length of these chains has no substantial influence on the optical properties. The photophysical properties were computed as vertical electronic excitations from the minima of the ground-state, using the linear-response approach, the B3LYP/6-31+G(d) level of theory and the first ten excited states. Using the optimized ground-state geometry for the starting coordinates, TD-DFT^[59] geometry optimization of the first excited singlet state (S1) was performed at the same level of theory. For all calculations, the solvent effect was taken into account by including the polarizable continuum model (PCM),^[60] and acetonitrile as solvent. All obtained minima were confirmed by the absence of a negative frequency in the vibrational analysis. Natural transition orbital (NTO)^[61] calculations were performed after TD-DFT calculations to describe the physical behaviour of holes and electrons in the excited states. Noteworthy, for all dves several conformations are possible. The herein reported data refer to the anti conformations shown in Scheme 1. The calculations done with other conformations did not yield significant differences, neither in energy nor for the calculated electronic and photophysical properties.

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Shine bright: Near-infrared twophoton excitation of bis(dioxaborines) with exceptional cross sections yields strong fluorescence. The rationally designed dyes with variable π conjugation belong to the brightest emitting two-photon absorbers with acceptor- π -acceptor architecture known to date. Alvaro Moneo Marín, João P. Telo, Daniel Collado, Francisco Nájera, Ezequiel Pérez-Inestrosa, and Uwe Pischel*

Bis(dioxaborine) Dyes with Variable π -Bridges: Towards Two-Photon Absorbing Fluorophores with Very High Brightness



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